On the Mobility of Atoms over the Surface of a Crystal at the Melting Temperature

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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On the Mobility of Atoms over the Surface of a Crystal at the Melting Temperature

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In thermodynamic calculations of a number of adsorption processes it has proved necessary, even at moderate temperatures, to take into account the entropy of two-dimensional translational motion of adsorbate molecules ([1]). At temperatures above $0.3T_{\mathrm{m}}$, mobility of surface atoms of crystals is manifested (see, for example, ([2])); in what follows this is called mobile autoadsorption. By mobile autoadsorption of atoms on the surface of platinum and palladium it has been possible to explain the peculiarities of their catalytic properties at high temperatures ([3-5]). The pre-exponential factors of the rate constants of a catalytic reaction, calculated with allowance for the entropy of two-dimensional mobility of the metal atoms, agree satisfactorily with the experimental values ([4]). In connection with the above, it is of interest to estimate the degree of mobility of atoms over the surface of crystals at the melting temperature.

Fig. 1. Diagram of a portion of a close-packed face:
1 —atom at a kink of a growth step; **2** —atom immobilely adsorbed on the face;
3 —atom immobilely adsorbed at a growth step

Experimental and theoretical studies of mass transfer between a crystal and vapor or melt have shown ([6]) that on crystal faces there exist incomplete layers one particle thick, whose edges are growth steps. Figure 1 schematically shows a portion of a close-packed face. The atoms of the upper layer are hatched. The positions of the surface atom, denoted by the numbers $1, 2, 3$, differ in the number of its bonds with other atoms. Let φ be the energy of the bond of a surface atom with an immediate neighbor, and φ' the energy of the bond with the next-nearest atom. The difference in the number of such bonds for two positions of the atom may be regarded as the change in enthalpy of the system per atom in the corresponding transition. The transition of an atom immobilely adsorbed on a face into the state of mobile autoadsorption is possible already when one or two bonds are weakened, without their rupture, as is shown in Table 1 by the factor $\alpha < 1$. The values of α depend on the nature of the

crystal and on the face considered; for a given substance they are constant only within each row of Table 1. To estimate the bond energy φ, we make the usual assumptions that ΔH_4^0 is equal to the heat of sublimation and that $\varphi \gg \varphi'$; the values of φ found for 28 metals at their melting temperatures are given in Table 2.

On transition of atoms from the bulk of the lattice to positions 1, 2, and 3 (Fig. 1), the entropy changes are small ([6],[7]). By contrast, transition to the state of mobile autoadsorption, in which two translational and one vibrational degrees of freedom relative to the lattice may be assigned to the atoms, will be accom-

Table 1

Changes in enthalpy for certain transitions of atoms

Lattice type	Face	ΔH_1^0	ΔH_2^0	ΔH_3^0	ΔH_4^0
Hexagonal close-packed A3	(0001)	3φ	$\alpha\varphi$	$3\varphi + \alpha\varphi$	$6\varphi + 3\varphi'$
Face-centered cubic A1	(111)	3φ	$\alpha\varphi$	$3\varphi + \alpha\varphi$	$6\varphi + 3\varphi'$
Face-centered cubic A1	(100)	$2\varphi + 2\varphi'$	$2\alpha\varphi$	$2\varphi(1+\alpha) + 2\varphi'$	$6\varphi + 3\varphi'$
Body-centered cubic A2	(110)	$2\varphi + \varphi'$	$\alpha(\varphi + \varphi')$	$\varphi(2+\alpha) + \varphi'(1+\alpha)$	$4\varphi + 3\varphi'$
Body-centered cubic A2	(100)	$2\varphi'$	$2\alpha\varphi$	$2(\varphi + \alpha\varphi)$	$4\varphi + 3\varphi'$

Note. ΔH_1^0–step kink–adsorption on a face; ΔH_2^0–adsorption on a face–mobile autoadsorption; ΔH_3^0–step kink–mobile autoadsorption; ΔH_4^0–step kink–vapor.

Table 2

Results of calculating the heat of transition of atoms from kinks of growth steps into the state of mobile autoadsorption for certain metals.

Lattice type	Element	m.p., °K	ΔS_T^0 m.p., e.u. min	ΔS_T^0 m.p., e.u. max	ΔH_T^0 m.p., kcal/g-at min	ΔH_T^0 m.p., kcal/g-at max	Bond energy φ, kcal/g-at	Number of broken bonds min	Number of broken bonds max
A2	U	1406	19,4	22,4	27,3	31,5	28,0	1,0	1,1
A2	Li	453,7	19,4	23,9	8,8	10,8	9,57	0,9	1,1
A2	Th	1968	19,0	21,6	37,3	42,4	32,5	1,1	1,3
A2	Rb	312	17,6	21,2	5,5	6,6	4,90	1,1	1,3
A2	Cs	301,8	17,0	20,5	5,1	6,5	4,65	1,1	1,4
A2	Tl	577	20,6	25,3	11,9	14,6	10,6	1,1	1,4
A2	Na	370,97	19,6	24,2	7,3	9,0	6,5	1,1	1,4
A2	K	336,4	18,1	22,1	6,1	7,4	5,35	1,1	1,4
A2	Hf	2250	22,5	26,8	50,6	60,5	41,4	1,2	1,5
A2	Zr	2125	21,5	25,2	45,6	53,5	36,0	1,3	1,5
A2	Nb	2770	22,8	27,0	63,0	74,8	44,0	1,4	1,7
A2	Ti	1950	21,0	24,6	41,0	48,0	27,0	1,5	1,8
A2	V	2190	22,0	25,9	48,2	56,6	29,6	1,6	1,9
A2	Fe	1812	21,2	25,0	38,4	45,3	23,5	1,6	1,9
A1	Pt	2043	23,2	27,3	47,4	55,9	22,0	2,2	2,5
A1	Au	1336	23,1	28,1	30,8	37,5	13,8	2,2	2,7
A1	Ni	1728	22,0	26,4	38,0	45,6	16,4	2,3	2,8
A1	Rh	2239	22,9	27,2	51,2	61,0	21,5	2,4	2,8
A1	Co	1768	21,9	25,4	38,7	44,9	16,3	2,4	2,8
A1	Cu	1356	23,1	28,1	31,3	38,2	13,2	2,4	2,9
A1	Ag	1234	22,6	27,4	27,9	33,8	11,1	2,5	3,0
A1	Ir	2727	23,7	28,2	64,6	77,1	24,4	2,7	3,1
A1	Pd	1823	22,8	27,2	41,5	49,6	15,2	2,7	3,2
A3	Ru	2700	24,2	29,0	65,3	78,2	23,7	2,8	3,3
A3	Os	3000	24,8	30,0	74,5	90,0	26,3	2,8	3,4
A3	Cd	594	21,4	26,6	12,7	15,5	4,37	2,9	3,5
A3	Zn	692,7	22,0	27,2	15,2	18,8	5,1	3,0	3,7
A3	Mg	923	21,3	25,7	20,0	23,7	5,75	3,4	4,1

be accompanied by a significant change in entropy. Taking into account the decrease in the strength of the bond of a mobile autoadsorbed atom with the lattice in comparison with an atom located at a site of the crystal lattice, one may suppose that, for an isotropic crystal, the frequency of such vibrations should be lower, and the anharmonicity higher, than for an atom in the bulk of the crystal lattice. Therefore the vibrational entropy of a mobile autoadsorbed atom should be higher than the entropy due to vibration along one normal coordinate of an atom located at a site of the crystal lattice. On the other hand, since the magnitude of the entropy indicates the degree of disorder in the

system, the entropy corresponding to one degree of freedom of any vibrational motion should be smaller than that for one degree of freedom of translational motion.

Thus, for an atom that has passed into the state of mobile autoadsorption, two degrees of freedom of vibrational motion are replaced by two degrees of freedom of translational motion, and the entropy of vibration of such an atom relative to the lattice lies between one third of the entropy of an atom in the bulk of the crystal at the given temperature and the entropy of one-dimensional po-

translational motion. The minimum standard change in entropy upon transition to the state of mobile autoadsorption is:

$$\min \Delta S_T^0 = {}_2S_T^0 - 0.67\,\kappa S_T^0. \tag{1}$$

Here ${}_2S_T^0$ is the standard entropy of two-dimensional translational motion of a mole of ideal gas at temperature T; κS_T^0 is the standard entropy of a mole of substance in the crystalline state at temperature T and external pressure of 1 atm. For the maximum change in entropy we obtain:

$$\max \Delta S_T^0 = {}_3S_T^0 - \kappa S_T^0, \tag{2}$$

where ${}_3S_T^0$ is the entropy of three-dimensional translational motion of a mole of ideal gas with molecular weight M at a pressure of 1 atm, which is determined as follows:

$${}_3S_T^0 = R \ln M^{3/2} T^{5/2} - 2.30. \tag{3}$$

The expression for the translational entropy of a two-dimensional gas has the form

$${}_2S_T^0 = R \ln MTA + 65.80, \tag{4}$$

where A is the area attributable to each adsorbed molecule. As the standard state of a two-dimensional gas, Campbell and Riedl ([8]) chose one in which the volume per mobile autoadsorbed molecule is equal to the volume per molecule in a three-dimensional gas at a pressure of 1 atm. Campbell and Riedl took the thickness of the adsorbed layer to be 6 Å; then, in the standard state, $A = 22.53T$ Å^2.

The standard entropy changes calculated by formulas (1)–(4) for the transition of $6 \cdot 10^{23}$ atoms from kinks of growth steps to the state of mobile autoadsorption are given in Table 2. It is easy to see that these quantities are close to the constant in Trouton' s rule, but for metals with the high-temperature lattice A2 the mean values $\min \Delta S_{T_\text{m}}^0 = 20 \pm 3$ and $\max \Delta S_{T_\text{m}}^0 = 24 \pm 3$ are somewhat

lower than for metals with lattices A1 and A3 ($\min \Delta S^0_{T_\text{m}} = 23 \pm 1$; $\max \Delta S^0_{T_\text{m}} = 28 \pm 1$).

It is easy to show that the pressure in the layer of mobile autoadsorption does not depend on the concentration of kinks of growth steps. Therefore this pressure can be estimated from the conditions of equilibrium between mobile-autoadsorbed atoms and atoms in the kinks of growth steps:

$$\ln p = \Delta S^0_T / R - \Delta H^0_T / RT. \tag{5}$$

Here p is expressed in atmospheres because of the choice, specified above, of the standard state in calculating ΔS^0_T by formulas (1)–(4); ΔH^0_T is the enthalpy change upon transition, under standard conditions, of $6 \cdot 10^{23}$ atoms from kinks of growth steps to the state of mobile autoadsorption.

It follows from Table 1 that, for different faces with low indices, the structure of which may be identical to the structure of undercoordinated layers on any surfaces of a given crystal, the transition of atoms from kinks of growth steps to the state of mobile autoadsorption is accompanied by the rupture of an unequal number of Me–Me bonds. This means that the equilibrium pressure of mobile-autoadsorbed atoms is different on crystalline layers that differ in structure. With decreasing packing density of the surface layer of a crystal, this pressure increases. For the A1 and A2 lattices, layers that are less dense than the other layers, the edges of which are growth steps, have the same structure as the (100) faces, and for the A3 lattice–as the (0001) faces. Therefore the changes in enthalpy upon the transition of $6 \cdot 10^{23}$ atoms from kinks of less densely packed growth steps to the state of mobile autoadsorption must be enclosed within the following limits:

$$\text{for the A2 lattice:} \quad \varphi \leqslant 2(\alpha\varphi + \varphi') \leqslant 2\varphi; \tag{6}$$

$$\text{for the A1 lattice:} \quad 2\varphi < 2\varphi(1+\alpha) + 2\varphi' \leqslant 3\varphi; \tag{7}$$

for lattice A3:

$$3\varphi < 3\varphi + \alpha\varphi < 4\varphi. \tag{8}$$

Substituting into inequalities (6)–(8) the values of φ at the melting temperature given in **Table 2**, and taking from the same table the values of $\Delta S^0_{T_\text{m}}$, one can, by formula (5), estimate for each metal the greatest pressure in the layer of mobile autoadsorption at the melting temperature. It turned out that this pressure is, in order of magnitude, close to 1 atm, independently of the nature of the metal and of the type of its lattice. Consequently, one may suppose the existence of the following equality:

$$T_{\text{m}} \cdot \Delta S^0_{T_{\text{m}}} = \Delta H^0_{T_{\text{m}}}, \tag{9}$$

where T_{m} is the melting temperature at an external pressure of 1 atm, while $\Delta S^0_{T_{\text{m}}}$ and $\Delta H^0_{T_{\text{m}}}$, when the standard state is chosen according to (8), are determined from relations (1)–(4) and (6)–(8), respectively.

By formula (9), the values of $\Delta H^0_{T_{\text{m}}}$ were calculated for 28 metals (see Table 2). The necessary thermodynamic data were taken from the handbook [9], and the high-temperature structures of the metals from the monograph [10]. Table 2 shows that the values of $\Delta H^0_{T_{\text{m}}}$ are indeed contained within the limits determined by inequalities (6)–(8).

It should be noted that the information on the crystalline structure of metals at temperatures close to T_{m} is in some cases contradictory. For example, chromium immediately after solidification has, according to some data [11], structure A1, and according to other data [12], structure A2. In the book by G. B. Bokii [13], the high-temperature structures indicated for thallium, titanium, and thorium are A1, and for hafnium—A3. The average numbers of bonds breaking during the transition of atoms from the kinks of growth steps into the state of mobile autoadsorption, found from these data, for all the indicated elements except titanium, did not agree with inequalities (7) and (8). When, however, the calculation was made for structure A2, which according to the monograph [10] all four of the indicated elements have at high temperatures, the results coincided with those predicted by inequality (6), while for titanium inequalities (6) and (7) are satisfied if it is regarded as belonging to the structural types A2 and A1, respectively. Conversely, for calcium, the expected value calculated for structure A3 [13] agrees better than that for structure A2 [10]. For beryllium, the indicated agreement takes place both for structure A3 [10, 13] and for structure A2 [12]; the same is true in the case of barium.

The foregoing shows that the pressure in the layer of mobile autoadsorption on the least densely packed surface layers, whose edges form the growth steps of the crystal, reaches a value of the order of 1 atm at the melting temperature. As a result, in some cases it becomes possible to predict the structure of crystals near the melting point if the melting temperature, heat of sublimation, and the dependence of heat capacity on temperature up to the melting point are known.

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Note: Figure translations are in progress. See original paper for figures.